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Behavior of Organic Pollutants during Rapid-Infiltration of Wastewater into Soils 1. Processes, Definition, and Characterization Using a Microcosm

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JOURNAL ARTICLE

Behavior of Organic Pollutants During Rapid-Infiltration of Wastewater Into Soil: I. Processes, Definition, and Characterization Using a Microcosm

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ABSTRACT

A microcosm was constructed to study the behavior of organic pollutants during rapid infiltration of municipal wastewater into soil. The microcosm permitted a direct measure of the amount of volatilization and allowed calculation of the amount that degraded. The microcosms received 4.4 ± 0.2 cm of wastewater each day; an application was made every four hours. The wastewater was amended with selected organic compounds at individual average concentrations of 0.2 to 32 µmol/L. Chloroform, 1,1-dichloroethane, 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene volatilized extensively. Individual average concentrations in the microcosm effluent ranged from 9 ± 5% to 27 ± 11% of the applied concentrations. There was observable degradation of 1,1-dichloroethane but there was no detectable degradation of the other volatile compounds. Small proportions of chlorobenzene, 1,2-dichlorobenzene, and toluene volatilized; the remaining portion was extensively degraded, producing concentrations in the volume effluent of 9 ± 10% of the influent concentration or less. The concentration of 1,2,4-trichlorobenzene in the column effluent was <0.7% of that applied. The proportion that volatilized was not measured. Degradation was extensive for nitrobenzene, phenol, 2-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol; concentrations in the column effluent were <0.2% of applied concentrations. The behavior of toluene and tetrachlorethene at ambient concentrations in wastewater (0.09 and 0.3 µmol/L) was similar to their behavior at amended concentrations.

INTRODUCTION

The undesirable constituents of municipal wastewater include a plethora of industrial organic compounds, usually present at trace concentrations [1, 2, 3, 4]. Occasionally, some of these compounds exceed acceptable limits for drinking water. For example, in a study of forty publicly-owned wastewater treatment plants, the flow-weighted average of trichloroethene and tetrachloroethene were 0.65 and 1.15 µmol/L. The U.S. EPA [6] has proposed a Recommended Maximum Contaminant Levels (RMCL's) of zero for trichloroethene and tetrachloroethene. RMCL's are nonenforceable health goals. The enforceable standard has not yet been established. Guidance to ensure adequate removals of toxic organic compounds is not provided by the current Process Design Manual for Land Treatment of Municipal Wastewater [7], even though the manual cites several field studies where adequate removal of these compounds was obtained. This probably reflects an inadequate technical basis for rational design.

Removal of the organic compounds from the soil solution can occur through sorption, transformation, and volatilization. Sorption of many of the identified organic compounds in wastewater can be adequately described by hydrophobic sorption theory [3 or 8]. However, volatilization and transformation are poorly defined and poorly described.

This study considers the role of transformation and volatilization in the behavior of selected organic pollutants in wastewater. Their behavior was monitored in a microcosm, which allowed a direct measure of the extent of volatilization, and facilitated a mass balance to estimate transformation. The microcosm was designed to simulate a rapid-infiltration land-treatment system. The term rapid infiltration land treatment was adopted to reflect the rate of waste water application [7]. By definition more than 5.3 $m \cdot yr^{-1}$(4 per wk) wastewater application is considered to be rapid infiltration regardless of the water distribution method or plant cover. It is anticipated that rapid infiltration is the land treatment system most likely to pollute ground water. To optimize removals requiring oxidizing conditions, the wastewater was scheduled to maintain unsaturated conditions. This paper describes the microcosm and the behavior of the organic pollutants. In Part II of this manuscript the actual behavior of the chemicals is compared to predictions based on the operation of the microcosm, the properties of the soil, the physical-chemical properties of the compounds, and the tendency of the compounds to be transformed.

MATERIALS AND METHODS

Design of Microcosms

A fine sandy soil from the Lincoln soil series, a mixed thermic typic Ustifluvent, was collected in 10 cm increments from a profile near Ada, Oklahoma (see Table 1). The soil was packed into seven borosilicate glass columns to a bulk density of 1.6 $Mg \cdot m^{-3}$. Each 10 cm increment was packed in the same relative position occupied in the original profile. The saturated hydraulic conductivity of the seven columns was 3.47 ± 0.29 $cm \cdot h^{-1}$. The average pore-water content of the soil (θ = 0.21) was determined from the retention volume of a slug of tritiated water. The air-filled porosity was calculated to be 0.19 m^3/m^3 by difference assuming the specific gravity of the soil was 2.65 $Mg \cdot m^{-3}$. To protect the soil biota, the soil was not dried or sieved, and the columns were packed soon after collection of the soil. The columns were planted to Reed Canary Grass. Temperature was maintained at 293 ± 2 °K (20 ± 2 °C).

The experimental configuration of the microcosms is shown in Fig. 1. Unless otherwise noted, all materials that contacted the wastewater, dose solution, soil, or effluents were either borosilicate glass or Teflon. The glass columns were 15 cm I.D. x 150 cm long with sampling ports at 7.5, 15, 30, and 60 cm. The ports were fitted with suction samplers composed of a cylinder of sintered glass 1 cm I.D. and 2 cm long. The samplers were positioned at the mid line of the soil columns. Their maximum pore size was 4 to 8 μm. To allow determination of the rate of volatilization of the compounds, the top of each column was enclosed in a "greenhouse" 45 cm high. Room air was flushed through the greenhouses at 1 ± 0.2 liters/min resulting in the replacement of the air in the greenhouses every 8 min. The flow rate was arbitrarily selected as an easily measurable quantity without exceeding mechanical limitations of the laboratory vacuum system. The greenhouses were illuminated with six G.E. Powergroove® cool white fluorescent lamps arranged in a semicircle of radius 30 cm about the center of the greenhouses. The microcosms were illuminated 12 h every day. The soil columns were wrapped in foil to prevent the growth of algae on the walls of the glass pipes.

Three of the columns received primary municipal wastewater from Ada, OK (Table 1). The wastewater was collected fresh daily and stored at 277°K (4°C) until use. The wastewater passed a short piece of silicone peristaltic-pump tubing on its way to the soil columns. Three of the columns received wastewater amended with a suite of organic chemicals (Table 2).

TABLE 1.
Characteristics of the Wastewater Applied to the Microcosms, of Renovated Wastewater in the Microcosm Effluent, and of the Soil in the Microcosm.†

		Wastewater Applied to microcosms		Column effluent	
Parameter	Unit	Mean	Range	Mean	Range
TOC	$mmol \cdot L^{-1}$	3.7	6.6 - 0.2	0.3	0.9 - 0.2
NO_3^- (N)	$mmol \cdot L^{-1}$	0.014	0.064-<0.004	0.69	2.9 - <0.004
NH_4^+ (N)	$mmol \cdot L^{-1}$	1.10	1.57 - 0.56	0.042	1.4 - <0.004
				(unamended microcosms)‡	
				0.30	1.1 - <0.004
				(amended microcosms)	
TKN (N)	$mmol \cdot L^{-1}$	1.64	2.23 - 0.8	0.11	2.08 - 0.02
				(unamended microcosms)	
				0.36	1.19 - 0.02
				(amended microcosms)	
PO_4^{-3} (P)	$mmol \cdot L^{-1}$	0.19		0.12	
SO_4^{-2}	$mmol \cdot L^{-1}$	0.90		0.82	
Cl^-	$mmol \cdot L^{-1}$	2.96		2.90	
O_2	$mmol \cdot L^{-1}$	-		0.04	
Alkalinity	$mmol \cdot L^{-1}$	4.1		3.4	
Conductivity	µS	1100		966	
pH		7.7		7.7	

† Lincoln fine sand: 92% sand, 5.9% silt, 2.1% clay, 0.087% organic carbon, CEC 3.5 mmolg/100g.
‡ Amended or unamended with organic chemicals.

A concentrated dosing solution of the organic chemicals was mixed with the wastewater at a ratio of 1 to 15 just prior to release to the soil columns. To minimize losses of the organic chemicals from volatilization or biodegradation in the dosing solution, the solution was prepared aseptically in filter-sterilized water and was stored without a headspace in sterile, flexible Teflon bags (Alltech Assoc., Arlington Heights, IL). Each bag was fitted inside a sealed glass container filled with water. Water was pumped into the container around the bag with a peristaltic metering pump, which forced the dosing solution from the bag into a chamber where it was mixed with wastewater. The amended wastewater was delivered to a soil column using a siphon. Compressed N_2 at 14 kPa was used to start the siphon. It was necessary to provide a vent controlled by a solenoid valve in the head space of the mixing chamber to permit operation of the siphon.

The sole water supply for the city of Ada is Byrd's Mill spring. To evaluate the influence of the organic materials and mineral nutrients in the wastewater on the behavior of the priority pollutants, the seventh column received Byrd's Mill spring water amended with organic compounds and nitrogen (0.7 µmol/L). The nitrogen was added to maintain plant growth similar to columns receiving wastewater. Without nitrogen, strong deficiency symptoms were observed in plant cover.

Each of the columns received 4.4 ± 0.17 cm of water each day. An equal application of wastewater was made every 4 h. It was not possible to maintain a continuous wastewater application of 8 cm/d without plugging the columns.

TABLE 2.
The Concentrations of Organic Pollutants in Amended Municipal Wastewater Actually Delivered to Microcosms, the Expected Concentrations, and the Concentrations of Organic Pollutants in the Influents of Municipal Wastewater Treatment Plants.

Compound	Microcosm study: Method of analysis†	Microcosm study: Expected‡ conc. (µmol/L)	Microcosm study: Observed conc.(µmol/l) $\bar{X}$	Microcosm study: Observed conc.(µmol/l) S	Microcosm study: Observed conc.(µmol/l) N	Publicly owned treatment plants (POTP): Moccasin Bend TP§ Max. conc. (µmol/L)	Moccasin Bend TP§ Avg. conc. (µmol/L)	40 POTP¶ Max. conc. (µmol/L)	40 POTP¶ Flow-weighed conc. (µmol/L)
Halogenated aliphatic hydrocarbons									
Chloroform	P&T	44.9	31.8	6.0	9	1.26	0.62	3.6	0.15
1,1-Dichloroethane	P&T	21.0	13.0	3.3	9	0.02	<0.01	0.24	
1,1,1-Trichloroethane	P&T	18.8	12.6	3.9	9	1.8	0.18	230	2.6
1,2-Dibromo-3-chloropropane	P&T	15.2	9.2	3.1	9				
Trichloroethene	P&T	22.6	8.3	2.3	9	1.9	0.18	14	0.65
Tetrachloroethene	P&T	22.8	2.6	0.7	9	2.7	0.34	34	1.2
Substituted benzenes									
Chlorobenzene	P&T	6.9	3.1	0.7	9	0.02	0.01	13	
	Ext.		1.9	0.5	19				
1,2-Dichlorobenzene	P&T Ext.	7.1	2.4	1.0	9	0.08	0.01	3.0	
1,2,4-Trichlorobenzene	Ext.	6.6	0.72	0.17	19	0.88	0.17	24	
Nitrobenzene	Ext.	5.2	2.2	0.56	20				
Toluene	P&T	6.9	2.9	0.76	9	17.4	3.5	140	3.1
Phenols									
Phenol	Ext.	6.8	4.6	1.2	15	7.7	2.6	14.9	0.7
2-Chlorophenol	Ext.	7.0	4.7	1.0	16			0.04	
2,4-Dichlorophenol	Ext.	6.9	4.8	1.2	14	0.19	0.03	0.15	
2,4,6-Trichlorophenol	Ext.	7.0	4.8	1.1	14	0.06	0.01	0.06	
Misc									
Diethylphthalate	Ext.	3.4	0.22	0.19	20	0.10	0.02	0.19	0.014
2-Chloroethylvinyl ether	P&T.	11.1	10.2	2.9	9			0.09	
Bis(2-chloroethyl) ether	Ext.	10.6	7.4	2.0	20				

†P&T = Purge and Trap, Ext. = Extraction with methylene chloride or XAD resin.
‡Based on the amount of chemical added to the concentrated dosing solution.
§U.S.EPA [4], plant located Chattanooga, TN
¶U.S.EPA [5]

Amending Wastewater with Organics

The concentrated dosing solution of organic chemicals was prepared from two stock cocktails containing mixtures of the neat compounds. The "volatiles" cocktail contained 1,1-dichloroethane, 1,1,1-trichloroethane, tetrachloroethene, trichloroethene, chloroform, toluene, 1,2-dibromo-3chloropropane, and 2-chloroethylvinyl ether. The "extractables" cocktail contained chlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, phenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, nitrobenzene, bis-(2-chloroethyl)-ether and diethylphthalate. To prepare the concentrated dosing solution, portions of the cocktails were taken into glass and Teflon syringes in a manner that sterilized the syringe and exterior of the needle with the cocktails. The portions were added to 2 L of filter-sterilized water that completely filled a glass erlenmeyer flask containing a ℁29/40 ground glass joint. The syringe needle was inserted below the water surface to prevent entrapment of any of the cocktail on the surface film of the water. After all droplets of the two cocktails had fallen below the neck of the ground-glass joint, a glass stopper was carefully inserted to minimize any entrapment of air below the stopper. The mixture was vigorously stirred with a magnetic spin-bar for 24 to 48 h to dissolve the compounds. The stopper was replaced with a sterile dip tube connected to a sterile Teflon bag in the storage reservoir for the concentrated dosing solution. Filtered air was used to drive the concentrated dosing solution into the bags. The water displaced from the rigid container was measured to determine the volume delivered to the bags. To prevent rupture the bags never received more than 350 ml, roughly two-thirds of their maximum capacity. The concentrated dosing solution in the reservoirs was replaced every three to four days.

Many of the organic compounds examined in this study have several relatively heavy halogen atoms per molecule. As a result the mass of these compounds is not an accurate estimate of the amount of metabolically important elements available. To compensate for this situation the quantities of each compound added to the concentrated dosing solution were such that, barring loss or failure to dissolve, the amended wastewater would contain 42 µmol/L (0.5 mg/L) of C for each compound.

Sampling and Analysis of the Microcosms

The compounds in the "volatiles" cocktail, plus chlorobenzene and 1,2-dichlorobenzene were analyzed essentially in accordance with EPA protocol method #601 [9]. For analysis of wastewater amended with chemicals and column effluent a Hewlett Packard 7675A Purge and Trap unit was used to purge a 10 ml sample onto a Tenax trap using nitrogen as the purge gas. The sample was purged for 12 min at a rate of 40 ml/min. The trap was then desorbed for 5 minutes at 473°K onto a 5880 Hewlett Packard gas chromatograph. A 20 minute vent at 523°K followed desorption. The internal standards were 1-bromo-3-chloropropane and 1-chlorohexane.

Air flowing through a greenhouse was sampled by removing the Tenax trap from the Purge and Trap unit and connecting it to a splitter at the effluent port of the greenhouse. The trap was protected from excess moisture by a small filter of Dri-Rite®. The greenhouse was sampled for 24 h. From 0.1 to 0.5% of the total flow through the greenhouse passed through the trap. Flow rates through the trap were measured both at the beginning and end of the sampling period using a soap film flow meter. Then the trap was replaced in the Purge and Trap unit. The internal standards were added to 10 ml distilled water and the water was purged and analyzed as described above. The instrument had been calibrated by purging known solutions of the compounds from water. As a result it was necessary to correct the detector responses from traps that sampled an air stream. The concentration reported reflects appropriate capture and purging efficiency corrections.

Water from the sampling ports was acquired with a gentle vacuum (30 kPa). Water was collected into 16 ml screw-cap test tubes; any volatiles that escaped were captured on a Tenax trap (Fig. 1). After approximately 10 mls were collected, the collector was removed from the port, the amount of water sampled was determined by increase in weight, and then additional water was added to the tube to chase

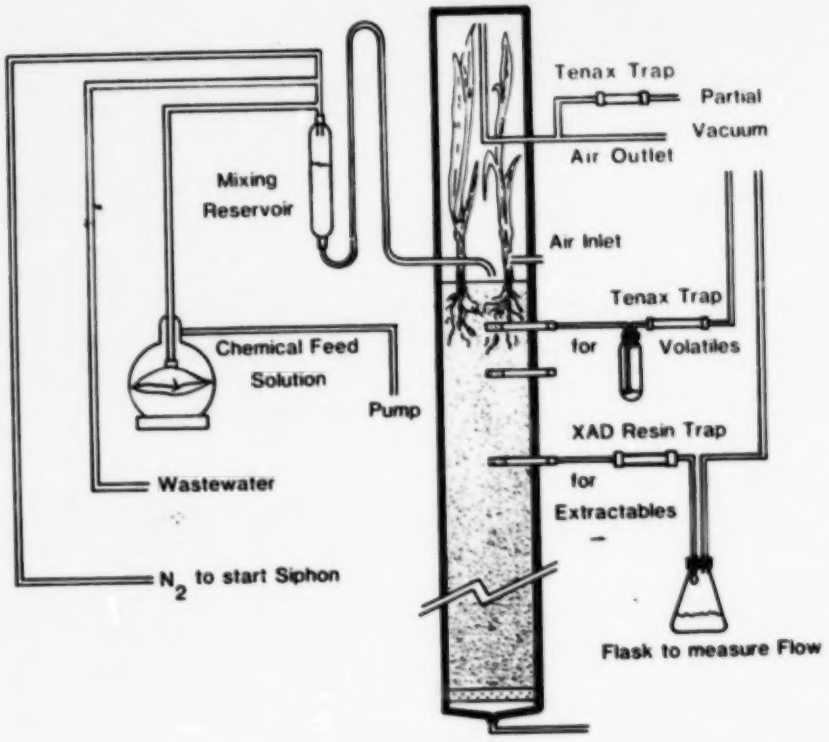

FIGURE 1.
A Microcosm to Simulate the Fate of Organic Contaminants in Municipal Wastewater Applied to Soil

to determine the retardation of phenols and diethylphthlate, the water was amended with 0.1% (w/v) NaN_3 to inhibit biotransformation of the compounds and did not contain any wastewater.

Sorption of the phenols was relatively unimportant based on their retardation factors, while diethylphthalate sorbed to a greater extent than expected (Table 3). An exposure of 12 weeks should have been adequate to bring all the compounds, except perhaps diethylphthalate, to steady-state. Both dosed and nondosed microcosms were sampled regularly over the subsequent 28 weeks. The concentration of the compounds actually achieved in the amended wastewater was appreciably less than that expected from the amount of chemical added to the concentrated dosing solution (Table 2). The achieved concentrations of the phenols, the alkanes, 2-chloroethylvinyl ether, and nitrobenzene were at least 50% of the expected. The achieved concentration of the alkenes was considerably less; however, it is known that these compounds can diffuse through the Teflon bag used in the storage reservoir. A comparison of the concentrations of compounds in fresh concentrated dosing solution, and in old dosing solution that was discarded before recharging the reservoirs, showed that concentrations of the phenols, nitrobenzene, and bis-(2-chloroethyl) ether were stable, while the concentrations of the chlorobenzenes declined 34% to 59% during 3 to 4 days storage. The cause of this decline is unknown. The achieved concentration of diethylphthalate was very low, only 6%

TABLE 3
Retardation of Selected Organic Pollutants in Lincoln Fine Sand

Compound	Expected retardation*	Determined retardation†
Phenol	1.1	1.1 ± 0.28
2-chlorophenol	1.1	1.4 ± 0.36
2,4-dichlorophenol	1.4	2.7 ± 0.64
2,4,6-trichlorophenol	2.2	1.3 ± 0.36
Nitrophenol	1.2	1.1 ± 0.59
Diethylphthate	2.2	>16

*After Wilson et al. 1981 using the equation of Chiou et al. 1979.
†Mean of three replicates ± 95% confidence interval.

NOTE: 2,4,6-trichlorophenol was present as the phenate ion at the experimental pH, which probably explains the poor correspondence between the determined retardation, and the expected retardation based on hydrophobic sorption assuming a unionized form.

of the expected concentratration and highly variable. This probably reflects analytical inconsistencies and a tendency for this compound to sorb to the glass flask used to dissolve the compounds.

The replicability of the achieved concentrations was good with the exception of diethylphthalate. The average of the coefficients of variation of concentrations was 0.28 for the purgeables and 0.30 for the extractables.

Table 2 presents average and maximum concentrations of organic contaminants encountered in a study of the Moccasin Bend plant in Chattanooga, TN [4] which was intensely monitored for 36 days, and in a survey covering 40 publicly-owned wastewater treatment plants [5]. The average concentrations of organic contaminants in the two studies were very similar, but the maximum concentrations encountered in the study of 40 plants were generally higher than those encountered in the Moccasin Bend plant alone.

In the microcosms, the concentration of the chlorobenzenes, the alkenes, 1,1,1-trichloroethane, and diethylphthalate were near the maximums encountered in the treatment plant monitoring studies. The concentrations of chloroform and 2,4-dichlorophenol were roughly 10 times the maximums encountered in the study of 40 plants, while the concentrations of 1,1-dichloroethane, 2-chlorophenol, 2,4,6-trichlorophenol and 2-chloroethyl vinyl ether were 100 times the maximum in the study of 40 plants. Concentrations of phenol and toluene were near the average of both monitoring studies. Nitrobenzene, bis (2-chloroethyl)ether and 1,2-dibromo-3-chloropropane occur rarely, if ever, in municipal wastewater. They were included as benchmark compounds for comparison to a previous study on the fate of organic compounds in soil that did not receive wastewater [8].

Fate of Organic Pollutants

The aliphatic hydrocarbons volatilized to an appreciable extent, resulting in substantial reductions in the concentrations of these compounds that would enter ground water (Table 4). Significant quantities of 1,2-dibromo-3-chloropropane and 1,1-dichloroethane could not be accounted for. This is most likely due to biotransformation, because the microcosms were at steady state with respect to sorption, and known rates of abiotic transformation processes such as hydrolysis could not account for the observed removal. There was no evidence for degradation of the other aliphatic hydrocarbons at rates that could be measured under the

experimental conditions. There was no significant difference in the behavior of these compounds in the microcosm that received spring water. The results are also in agreement with an earlier study on the behavior of these compounds in the absence of wastewater [7].

Ethylbenzene, which was commonly found in the unamended wastewater (Table 5), coeluted with 1,2-dibromo-3-chloropropane (DBCP) in the GC analysis of the traps sampling volatiles in the "greenhouses". Calculations, based on the model described in Part II, suggest that 80% of the ethylbenzene should volatilize from the soil surface. For this reason, there is potential for considerable interference in the measurement of DBCP volatilization. Fortunately, ethylbenzene degraded in the soil before the water reached the first sampling port (data not shown) and ethylbenzene should not have interfered with the measurement of DBCP in the soil solution.

The substituted benzenes were removed to a greater extent. Some of the material volatilized, and the remainder was extensively degraded. This probably results from biological attack; these compounds are biodegradable under aerobic conditions [10]. In the first three weeks after monitoring began, 1,2-dichlorobenzene appeared at concentrations of 0.14 to 0.07 μmol/L, roughly 10% of the applied concentration, in the effluent of the microcosm that received spring water. The concentration then fell below the detection limit of 0.0007 μmol/L. This may reflect a gradual adaptation of the microbiota to this compound in soil that received spring water amended with nitrogen. The compound was never detected in effluent from the soil that received wastewater. The behavior of the other substituted benzenes in the microcosm that received spring water was indistinguishable from the microcosms that received wastewater.

In the earlier study, the compounds were dissolved in spring water, not municipal wastewater, and degradation of the substituted benzenes was much less extensive. In that study, at least 23% of applied chlorobenzene, 1,4-dichlorobenzene and 1,2,4-trichlorobenzene passed through the soil, and nitrobenzene hardly degraded at all in two of three replicate soil columns. In this study, extensive degradation of the chlorobenzenes also occurred in the microcosm receiving spring water, which was amended with ammonium nitrate, indicating that the increased degradation was not exclusively associated with constituents of the wastewater. Either the plant roots, or more likely, higher concentrations of nitrogen promoted degradation.

The phenols were extensively degraded. Their concentrations dropped at least three orders of magnitude after passage of the wastewater through soil. There was no difference in behavior in spring water and wastewater, and no indication of a lag in degradation. For comparison, the fate of the phenols was also determined under the conditions of the earlier study. Again the concentration of the phenols was invariably less than the detection limit (0.008 μmol/L or 0.2% of applied concentration), indicating that degradation of these compounds was not limited by nitrogen availability or rhizosphere effects, as was the case with the chlorobenzenes.

The concentration of diethylphthalate in the effluent from the microcosms was generally below the detection limit. However, in the first and third month of monitoring this compound was sporadically detected in the effluent from all the microcosms, often at concentrations that greatly exceeded the applied concentrations. Diethylphthalate is a plasticizer in a number of products widely used in our laboratory and the occurrence of the compound in the effluent may have been due to contamination. Because the retardation of diethylphthalate in the Lincoln fine sand could not be measured (Table 3), it is impossible to determine whether the removal of this compound was due to sorption or biodegradation. In any case, removals during most of the monitoring period appeared to be extensive.

The removal of 2-chloroethylvinyl ether during passage through the microcosms was comparable to that of the halogenated aliphatic hydrocarbons. A compound in samples of volatiles from the "greenhouses" on columns receiving unamended wastewater coeluted with 2-chloroethylvinyl ether. The compound was not found in the applied wastewater or any of the soil solution samples in columns unamended with organics. The compound was not identified but apparently is a volatile degrada-

TABLE 4
Fate of Organic Compounds in Microcosms Simulating High-Rate Application of Municipal Wastewater to Land (Amended Concentrations).

Compound	Received wastewater			Rec'd spring water
	Volatilized	Microcosm effluent	Not accounted for	Microcosm effluent
	-- % of compound added --			
Halogenated aliphatic hydrocarbons				
Chloroform	75 ± 19†	27 ± 11†	-2 ± 17†	38
1,1-Dichloroethane	54 ± 15	27 ± 9	19 ± 12	30
1,1,1-Trichloroethane	89 ± 20	16 ± 8	-4 ± 22	5.7
Trichloroethene	77 ± 33	16 ± 11	7 ± 40	8.1
Tetrachloroethene	94 ± 72	9 ± 5	-3 ± 74	2.3
1,2-Dibromo-3-chloropropane	6‡	26 ± 18	68	34
Substituted benzenes				
Chlorobenzene	14 ∓ 7	3 ± 3	84 ± 7	<1
1,2-Dichlorobenzene	21 ± 12	<1	79 ∓ 12	<1
1,2,4-Trichlorobenzene	89§	<0.7	?	<0.7
Toluene	20 ± 18	9 ± 10	71 ± 20	13
Nitrobenzene	<0.1§	<0.1	>99.9	<0.1
Phenols				
Phenol	<0.1§	<0.1	>99.8	<0.1
2-Chlorophenol	<0.2§	<0.1	>99.7	<0.1
2,4-Dichlorophenol	<0.1§	<0.2	>99.7	<0.2
2,4,6-Trichlorophenol	<0.1§	<0.1	>99.8	<0.1
Misc.				
Diethylphthalate	0.5§	>100 to <2	?	>100 to <2
2-Chloroethylvinyl ether	3‡	16 ± 22	?	19
bis(2-chloroethyl) ether	3§	64 ± 6	?	49

† Means ± 95% confidence interval.
‡ Value presented is calculated instead of measured due to coelution with other compounds. See Part II of this manuscript for method of calculation.
§ The value presented was calculated from Part II of this manuscript. The amount that volatilized could not be measured directly.

tion product of something in the applied wastewater. As a result, an analytically determined mass balance for 2-chloroethylvinyl ether was not possible. However, calculations based on the methods in Part II of this manuscript indicate that the amount that volatilized should be small, and that considerable material is missing. It is likely the material degraded abiotically. In other work in our laboratory, 2-chloroethylvinyl ether also disappeared in deeper subsurface material that was similar to the Lincoln fine sand. Autoclaving had little effect on the rate of disappearance of the compound in this material (data not shown).

A small amount of bis (2-chloroethyl)ether may have been removed by passage through the soil; however, the amount removed is environmentally trivial.

The fate of ambient concentrations of selected organic compounds was monitored in three of the microcosms. The behavior of the compounds at ambient concentrations (Table 5) was similar to their behavior at the higher amended concentrations (Table 4). The concentration of 1,1,1-trichloroethane and trichloroethene was reduced at least an order of magnitude. The concentration of tetrachloroethene was only reduced three-fold; however, the confidence interval of the concentration

TABLE 5
Fate of Organic Compounds in Microcosms Simulating High-Rate Application of Municipal Wastewater to Land (Ambient Concentrations).

Compound	Wastewater			Microcosm effluent		
	Conc. (µmol/L)		Number of times detected (16 samples)	Conc. (µmol/L)		Number of times detected (60 samples)
1,1,1-Trichloroethane	0.09	(2.4)†	6	<0.002		0
Trichloroethene	0.05	(1.7)	12	<0.003		1
Tetrachloroethene	0.1	(2.1)	8	0.04	(4.7)	3
Toluene	0.3	(3.3)	16	0.05	(1.6)	8
Ethylbenzene	0.1	(4.9)	11	<0.003		0
Styrene	0.3	(3.2)	11	0.01	(2.9)	5
Isopropylbenzene	0.09	(3.7)	10	<0.0006		1

† Geometric mean (standard deviation)

in the column effluent is so wide a comparison has no statistical validity. Toluene and styrene were reduced during passage through the microcosms, while ethylbenzene and isopropylbenzene degraded extensively.

Comparison to Other Systems

If a land treatment system is operated in a manner that keeps the soil unsaturated and thus in communication with the atmosphere, it can remove organic contaminants from municipal wastewater very effectively. Demirjian et al. [11] found that spray irrigation of wastewater that had been impounded in a lagoon provided such extensive treatment that the concentration of almost every organic contaminant was below the detection limit in the under drainage. Similarly, in a pilot-scale model of slow-rate land treatment, Jenkins and Palazzo [12] and Parker et al. [13] found very high removals of all the compounds they examined. The rate of application (5 cm in a day, one day a week) was approximately one-sixth the rate used in this study. Consequently there was more time for volatilization and/or transformation. As a result, the fraction of applied organic materials that passed through the soil was roughly an order of magnitude lower in their study than in this one (Table 6). When allowance is made for the different infiltration rates, the behavior of the two systems is in reasonable agreement. However, there is little agreement between the behavior of the organic contaminants among the three rapid infiltration studies. The higher application rates generally showed poor removals (Table 6).

Further work on the dynamics of redox changes in soil after flooding with municipal wastewater and the dynamics of microbial accommodation to flooding, would allow optimization of application schedules for removal of organic contaminants during land application of municipal wastewater to the soil.

SUMMARY AND CONCLUSIONS

The soil column microcosm, constructed to simulate rapid infiltration treatment of municipal wastewater, was shown to function in an acceptable manner. Using intermittent application of wstewater amended with a suite of hazardous organic compounds at rates representative of field-scale systems, the column was maintained under aerobic, unsaturated flow conditions. The greenhouse functioned adequately to permit quantitative estimates of volatilization rates from the top

TABLE 6
Effect of Scheduling and Rate of Application on the Removal of Organic Contaminants from Municipal Wastewater During Passage Through Soil.

	Slow rate*		Rapid Infiltration					
			16 m yr^{-1} 6 hr cycle†		90 m yr^{-1} 4 wk cycle§		14 day	
	Fraction remaining	Final conc. (nmol/L)	Fraction remaining	Final conc. (nmol/L)	Fraction remaining	Final conc. (nmol/L)	Fraction remaining	Final con (nmol/L
Refractory Compounds								
Chloroform	3.8%	6	27%	9,000	39%	9	–	–
1,1,1-Trichloroethane	–	–	16%	2,000	56%	12	–	–
Tetrachloroethene	0.4%	0.5	9%	200	197%	31	16%	1
Degradable Compounds								
Chlorobenzene	0.1%	<0.3	3%	90	–	–	–	–
1,2-Dichlorobenzene	–	–	<1%	<25	75%	18	17%	0.3
1,3-Dichlorobenzene	0.1%	<0.07	–	–	42%	2	–	–
1,4-Dichlorobenzene	–	–	–	–	67%	10	–	–
Toluene	<0.5%	<1	16%	0.5¶	–	–	–	–
Ethylbenzene	–	–	<21%	0.03¶	47%	0.8	–	–
Styrene	–	–	30%	0.9¶	<8%	0.2	–	–
Naphthalene	<0.7%	<2	–	–	32%	0.6	130%	0.4

*Jenkins and Palazzo, [12]; Parker et al., [13]. Windsor soil.
†This study.
‡Bouwer et al., [1]; Bouwer and Rice, 1984. First period.
§Hutchins et al., [15]. Second inundation.
¶Received ambient concentrations of organic contaminants in municipal wastewater.

of the soil column. Bottom and side port collection of column effluent, coupled with mass balance calculations, facilitated observations of degradation, both abiotic and biological, within the soil column for a number of the applied organics and several compounds occurring in the municipal wastewater.

As expected, many of the so-called volatile organics showed considerable volatilization losses in the application process; 1,1,1-trichloroethane and tetrachloroethene losses were about 90%. These volatile compounds, however, did not appear to degrade during passage through the column. In contrast, the substituted benzenes and phenols were degraded to the analytical detection limit during column passage. This is consistent with literature accounts of aerobic biotransformation of many of these compounds. Addition of nitrogen to some of the columns stimulated the microbial degradation of some of these organics. Effluent concentrations of the organic ethers also showed degradation, but to a lesser extent suggestive of an abiotic mechanism.

The potential utility of the soil column microcosm in optimizing design criteria for rapid infiltration treatment systems and evaluating the effectiveness of treatment of specific hazardous organic pollutants is demonstrated in this study. A more thorough mathematical interpretation of the results follows in Part II.

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